

**UNITED STATES AIR FORCE
RESEARCH LABORATORY**

**PERCHLORATE ANALYSIS BY AS-16
SEPARATION COLUMN**

David T. Tsui, Capt., USAF

Rebecca A. Clewell

J. Eric Eldridge, 2Lt, USAF

David R. Mattie, Ph.D.

**OCCUPATIONAL AND ENVIRONMENTAL HEALTH
DIRECTORATE**

**TOXICOLOGY DIVISION, ARMSTRONG LABORATORY
WRIGHT-PATTERSON AFB OH 45433-7400**

October 1999

Interim Report - February 1998 - July 1999

20060630318

**Human Effectiveness Directorate
Deployment and Sustainment Division
Operational Toxicology Branch
2856 G Street
Wright-Patterson AFB OH 45433-7400**

Approved for public release; distribution is unlimited.

STINFO COPY

NOTICES

When US Government drawings, specifications or other data are used for any purpose other than a definitely related Government procurement operation, the Government thereby incurs no responsibility nor any obligation whatsoever, and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data is not to be regarded by implication or otherwise, as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

Please do not request copies of this report from the Air Force Research Laboratory. Additional copies may be purchased from:

National Technical Information Service
5285 Port Royal Road
Springfield, Virginia 22161

Federal Government agencies and their contractors registered with the Defense Technical Information Center should direct requests for copies of this report to:

Defense Technical Information Service
8725 John J. Kingman Rd., Ste 0944
Ft. Belvoir, Virginia 22060-6218

DISCLAIMER

This Technical Report is published as received and has not been edited by the Technical Editing Staff of the Air Force Research Laboratory.

TECHNICAL REVIEW AND APPROVAL

AFRL-HE-WP-TR-1999-0240

This report has been reviewed by the Office of Public Affairs (PA) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.

FOR THE DIRECTOR



STEPHEN R. CHANNEL, Maj, USAF, BSC
Branch Chief, Operational Toxicology Branch
Air Force Research Laboratory

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.				
1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE October 1999	3. REPORT TYPE AND DATES COVERED Interim Report - February 1998 - July 1999		
4. TITLE AND SUBTITLE Perchlorate Analysis by AS-16 Separation Column		5. FUNDING NUMBERS Contract F41624-96-C-9010 PE 62202F PR 7757 TA 7757A2 WU 7757A210		
6. AUTHOR(S) Tsui, D.T., Eldridge, J.E., Mattie, D.R., and Clewell, R.A.				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Human Effectiveness Directorate Air Force Research Laboratory Wright-Patterson AFB, OH 45433-7400		8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Human Effectiveness Directorate Air Force Research Laboratory Wright-Patterson AFB, OH 45433-7400		10. SPONSORING/MONITORING AGENCY REPORT NUMBER AFRL-HE-WP-TR-1999-0240		
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) A new ion chromatography method was developed for perchlorate analysis using a Dionex AS-16 Separation Column. The AS-16 method proved to be more sensitive and selective than either the AS-5 or the AS-11 method, with a method detection limit for perchlorate of 0.19 ug/L. The higher capacity of the AS-16 analytical column allows trace level perchlorate to be detected in samples that could not be analyzed with either of the previous ion chromatography methods, due to the high concentrations of inorganic and organic contaminants. The method was shown useful in analyzing environmental samples that contained up to 15,000-ppm total dissolved solids, as compared to the AS-11 method, which could not detect perchlorate in samples containing 7,000-ppm total dissolved solids. A sample preparation method was also developed in order to remove interference ions, which can block the perchlorate signal to the detector. This preparation method reduces the background noise and increases the sensitivity of perchlorate analysis in environmental and industrial matrices.				
14. SUBJECT TERMS Perchlorate Ion Chromatography Sample Preparation			15. NUMBER OF PAGES 40	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL	

THIS PAGE INTENTIONALLY LEFT BLANK.

PREFACE

This report summarizes research that began in February 1998 and was completed in July 1999 under Department of the Air Force Contract No. F41624-96-C-9010. Major Steve Channel served as Contract Technical Monitor for the United States Air Force, AFRL/HEST.

TABLE OF CONTENTS

SECTION	PAGE
PREFACE.....	iii
TABLE OF CONTENTS.....	iv
LIST OF FIGURES AND TABLES.....	v
ABBREVIATIONS	vii
SECTION I: INTRODUCTION.....	1
SECTION II: MATERIALS AND METHODS	4
Test Materials.....	4
Reagents.....	4
Calibration and Control Standards.....	5
Instrumentation and Analytical Method	5
Effects of Sample Preparation Method on Mixed Anions	5
SECTION III: RESULTS	8
Method Development and Validation.....	8
Effects of KOH Mobile Phase on Perchlorate Retention Time and Response	13
Effects of Sample pH on Perchlorate Recovery and Retention Time.....	17
Interference Study	20
Application of AS-16 Method	23
Effects of Sample Preparation Method on Perchlorate Retention Time and Recovery	25
Effect of Sample Preparation on Interference Anions	26
SECTION IV: DISCUSSION AND CONCLUSIONS	29
SECTION V: REFERENCES.....	32
SECTION VI: ACKNOWLEDGEMENTS.....	33

LIST OF FIGURES AND TABLES

	Title	Page
Table 1.1.	Solubility of inorganic salts of silver.....	3
Table 2.1.	List of inorganic reagents and suppliers	4
Table 3.1.	Method detection limit data for perchlorate analysis on an AS-16 column	9
Table 3.2.	Effects of KOH mobile phase strength on 100-ppb perchlorate retention time, area count, and peak-height at 1.0 mL/min	13
Table 3.3.	Effects of KOH mobile phase strength on 100-ppb perchlorate retention time, area count, and peak-height at 1.5 mL/min	15
Table 3.4.	Effects of NaOH concentrations on 50-ppb perchlorate response and retention time on an AS-16 column, 1.25 mL/min, and 35-mM OH mobile phase	17
Table 3.5.	Effects of HCl concentrations on 50-ppb perchlorate response and retention time on an AS-16 column, 1.25 mL/min, and 35-mM OH mobile phase	17
Table 3.6.	Retention times of common inorganic anions on AS-16 column.....	20
Table 3.7.	Effect of ppm levels of carbonate, nitrate, chloride, and sulfate anions on 50-ppb perchlorate recovery on the Dionex Ion Pac AS16 column	23
Table 3.8.	Analysis of IPSC Samples by AS-16 Method	24
Table 3.9.	Effects of Millipore Millex-HV13 Filter on 25 and 100-ppb perchlorate spike recovery	25
Table 3.10	Effects of Ag- and H-On Guard cartridges and Millipore Millex HV- 13 filter on 25 and 100 ppb perchlorate spike recovery.....	26
Table 3.11	Results for Mixed Anion Removal Study Using On Guard Cartridges.....	27
Table 3.12	Results for Individual Anion Removal Study Using On Guard Cartridges.....	28

Figure 3.1.	Calibration curve generated from standard curve shown in Figure 3.2.....	10
Figure 3.2.	A Stack plot of 5 to 1000- $\mu\text{g/L}$ perchlorate calibration standards on an AS-16 column.....	11
Figure 3.3.	A Stack plot of 5 to 1000- $\mu\text{g/L}$ perchlorate calibration standards on an AS-11 column.....	12
Figure 3.4.	Elution profile of 100-ppb perchlorate on an AS-16 column on an AS-16 column, 1.0 mL/min at 25, 35, and 50-mM KOH mobile phase.....	14
Figure 3.5.	Elution profile of 100-ppb perchlorate on an AS-16 column on an AS-16 column, 1.5 mL/min at 25, 35, and 50-mM KOH mobile phase.....	16
Figure 3.6.	Elution profile of 50-ppb perchlorate spiked in various NaOH concentrations on an AS-16 column with 35-mM OH mobile phase flowing at 1.25 mL/min.....	18
Figure 3.7.	Elution profile of 50-ppb perchlorate spiked in various NaOH concentrations on an AS-16 column with 35-mM OH mobile phase flowing at 1.25 mL/min.....	19
Figure 3.8.	Effects of 1.0 mM trichloroacetic acid on the chromatography and detector response of 50-ppb perchlorate on an AS-16 column with 35 mM NaOH, 1.25 mL/mL.....	22

LIST OF ABBREVIATIONS

$^{\circ}\text{C}$	degrees Celsius
cm	centimeter
g	grams
HPLC	high performance liquid chromatography
IC	ion chromatography
ISE	ion selective electrode
L	liter
M Ω	mega-ohms
mA	mili-amperes
ml	mili-liter
mm	mili-meter
mmol	mili-mole
mM	mili-molar
mV	mili-volt
min	minutes
ppb	parts per billion
ppm	parts per million
TDS	total dissolved solid
μg	micro-gram
μm	micro-meter
μS	micro-siemen
UV	ultra violet
V	Volts

Perchlorate Analysis By AS-16 Anion Separation Column

SECTION I: INTRODUCTION

Perchlorate is a powerful oxidizer used in solid-rocket propellant mixtures, fireworks, and munitions. The presence of trace level perchlorate in drinking water poses a potential health risk, resulting from perchlorate's ability to interfere with the thyroid gland's uptake of iodide to produce thyroid hormones. The current EPA's recommended acceptable level for perchlorate in drinking water is 18 parts per billion (ppb). Since perchlorate is better known for its commercial and industrial applications, past occurrence studies have focused on water wells near regions where munitions, aerospace components, and fireworks were manufactured, developed and tested. Perchlorate has been reported in drinking water sources in the states of California, Utah, Nevada, West Virginia, and Texas.¹⁻⁶ However, recent reports have suggested that naturally occurring perchlorate is also present in fertilizers, nitrate deposits from northern Chile, and minerals from arid environments. These new findings have sparked intense efforts in the study of natural perchlorate occurrence in non-aqueous matrices, and in the development of new methodologies to support these studies.

The determination of perchlorate in drinking water at low (ppb) levels is a difficult analytical task. Ion chromatography (IC) is currently accepted to be the best available technology for perchlorate analysis in drinking water.^{7, 8} In 1997, the California Department of Health Services (CDHS) developed an IC method for the determination of trace level perchlorate in drinking water.⁹ The method utilized a Dionex IonPac[®] AS-5 column, a mobile phase consisting of 120-mM sodium hydroxide and 2-mM p-cyanophenol, and suppressed conductivity detection with an Anion MicroMembrane Suppressor. The method detection limit, when using a 740- μ L injection loop volume, was determined to be 4 ppb. In April 1998, the Dionex Application Laboratory developed an improved IC method for perchlorate analysis.^{10, 11} This method uses a 1 mL injection loop volume with an IonPac AS-11 column, 100-mM hydroxide eluent, and suppressed conductivity detection with an Anion Self-Regenerating Suppressor (ASRS). The AS-11 method detection limit was reported to be 1 ppb. The performances of both methods for drinking water matrix were validated in by inter-laboratory collaborative study, sponsored by the

Interagency Perchlorate Steering Committee (IPSC). For drinking water, the study found no differences between the two methods in terms of bias and accuracy.

The detection of perchlorate in complex environmental, industrial, and wastewater matrices poses an even greater challenge than that of drinking water, inviting difficulty from matrix effects, the presence of organic solvents, and high levels of total dissolved solid (TDS). In addition to the method validation, the IPSC collaborative study also evaluated the application of ion chromatography to trace level perchlorate analysis in a variety of environmental and occupational matrices. The collaborative study showed that high TDS concentrations limit the application of ion chromatography for the detection of low level perchlorate, at or near the method detection limit of 4 ppb, in water. Neither the AS-5 nor the AS-11 method was robust enough to be used with confidence in non-drinking water matrices. Both the electrical conductivity and TDS values for a given sample were defined as an essential prescreening measure. Furthermore, it was determined that preparative techniques for the removal of dissolved solids should be further investigated for the cases where TDS may pose a problem for IC analysis.

The purpose of this study is to develop a method for perchlorate analysis that would be applicable in non-drinking water matrices, such as wastewater, fertilizers, leafy vegetables, and mineral deposits, where the current methods fail. Intra-laboratory studies were performed to evaluate the ability of the Dionex AS-16 Separation column to account for the specific difficulties encountered when analyzing low level (ppb) perchlorate in various environmental and industrial matrices. The effects of solvents, eluent strengths, and the proposed sample preparation method were measured in order to compare the efficiency and sensitivity of the AS-16 method to those of the recommended AS-11 and AS-5 methods.

Environmental and industrial wastewater samples are likely to contain a variety of organic solvents, which can affect the analysis of perchlorate by altering the retention time, the sensitivity to perchlorate, and the life of the column. In order to compensate for these effects, a method was developed for perchlorate analysis with the Dionex AS-16 ion exchange column that would be more sensitive and have a longer column lifetime. As opposed to the AS-11 column, the AS-16 is specially designed for use with polarizable anions, which would theoretically

increase the sensitivity of the method for perchlorate. The AS-16 was also designed to have a higher capacity for exchange than previous columns. This higher capacity should prevent the organic solvents, such as methanol, from binding to the backbone of the resin and reducing the lifetime of the column.

For those environmental and industrial samples containing high TDS concentrations, a sample preparation method was developed that would allow the detection of low level perchlorate with ion chromatography. The sample preparation method was based on the unusually high solubility of perchlorate salts. It was determined that the silver salt of perchlorate would remain in solution, while most of the interference anions would precipitate out as the silver salts (Table 1.1). In order to prevent any silver from remaining in the sample during analysis, a silver saturated resin was used to facilitate cation exchange. As the water sample passed through the resin, the silver would bind with the interference anions to form the insoluble salts, and the dissolved cations would exchange onto the available sites on the resin. The solid salts could then be filtered out of solution. In this way, the background conductivity could be dramatically reduced, and any excess silver would remain on the resin. The decreased background noise should yield increased sensitivity and improved method detection limits for perchlorate analysis.

Table 1.1. Solubility of inorganic salts of silver

Salts	Solubility (g/100 mL 4 °C water)	Solubility (ppm in 4 °C water)
AgClO ₄	557	5570
AgNO ₃	122	1220
AgClO ₃	10	100
Ag ₂ SO ₄	0.57	5.7
AgBrO ₃	0.196	1.96
AgNO ₂	0.155	1.55
Ag ₃ PO ₄	6.5×10^{-4}	6.5×10^{-3}
AgCl	8.9×10^{-5}	8.9×10^{-4}
AgBr	8.4×10^{-6}	8.4×10^{-5}
AgI	$2.8 \times 10^{-7.25}$	$2.8 \times 10^{-6.25}$

SECTION II: METHODS AND MATERIALS

Test Materials

Primary source of perchlorate was ammonium perchlorate (lot # 03907LF) purchased from Aldrich-Sigma Chemical Company (St. Louis, MO). Secondary ammonium perchlorate (lot # K15G11) check standards were purchased from Alpha Chemical Company (Ward Hill, MA). Test materials were used without further purification.

Reagents

The eluent used was sodium hydroxide. Reagent grade sodium hydroxide was purchased from Aldrich-Sigma Chemical Company. Type I reagent water (18.0 to 18.3 MΩ/cm) was collected from a Barnstead Model D4751 Ultra Pure water system. Inorganic reagents and suppliers used in the interference study are shown in Table 2.1.

Table 2.1. List of inorganic reagents and suppliers

Reagent	Purity	Supplier
Arsenate	Reagent grade	J. T. Baker
Arsenite	Reagent grade	Fisher Scientific
Sodium Bromate	Reagent grade	Aldrich
Sodium Bromide	Reagent grade	Sigma
Sodium Carbonate	Reagent grade	Sigma
Sodium Chlorate	Reagent grade	Sigma
Sodium Chloride	Reagent grade	Fisher
Potassium Chromate	Reagent grade	Aldrich
Potassium Cyanide	Reagent grade	Sigma
Sodium Humate	Technical Grade	Aldrich
Potassium Iodate	Reagent grade	Aldrich
Potassium Iodide	Reagent grade	Sigma
Ammonium Molybdate	Reagent grade	Sigma
Ammonium Nitrate	Reagent grade	Sigma
Sodium Nitrite	Reagent grade	Aldrich
Potassium Phosphate	Reagent grade	Sigma
Phthalate	Reagent grade	Sigma
Sodium Selenate	Technical grade	Sigma
Potassium Sulfate	Reagent grade	Sigma
Sodium Sulfite	Reagent grade	Fisher
Potassium Thiocyanate	Reagent grade	Sigma
Sodium Thiosulfate	Reagent grade	Sigma

The following organic reagents were purchased from Supelco-Aldrich-Sigma Company: 1,1,1-trichloroethane, 1,1-dichloroethane, 1,2-dibromomethane, 1,2-dichloroethane, bromochloromethane, dibromochloromethane, dichlorobormomethane, dichloromethane, trifluoromethane, trichloroethylene, bromoform, chloroform, methanol, ethanol, freon 113, methylethylbutyl ketone, methylisobuthylketone, methyltertbutylketone, carbon tetrachloride, methylene chloride, methethylbenzene, ethylbenzene, benzene, m-, p-, o-xylene, styrene, and toluene. Haloacetonitriles (dichloroacetonitrile, dibromoacetonitrile, bromochloroacetonitrile, trichloroacetonitrile, 1,1 Dichloropropanone, 1,1,1Trichloropropanone) and haloacetic acids (monobromoacetic acid, dichloroacetic acid, trichloroacetic acid, dibromoacetic acid) were graciously provided by Dr. Sanwat Chaudhuri (Utah Department of Health, Division of Epidemiology and Laboratory Services, Salt Lake City, UT).

Calibration and Control Standards

Ammonium perchlorate stock standard solutions at 50-mg/ml were prepared gravimetrically (Metler Model PE-360 analytical balance, ± 0.0001 g) from pure neat standards. 1000- μ g/L working standard-solutions were prepared from the individual stock standard solutions. From the working standard-solutions, calibration or control standards at 5, 10, 25, 50, 100, 200, and 500- μ g/L were prepared by serial dilution.

Stock solutions of BrO_3^- , Cl^- , ClO_3^- , I^- , PO_4^{3-} , NO_2^- , NO_3^- , CO_2^- , SO_3^{-2} , $\text{S}_2\text{O}_3^{-2}$ and SO_4^{-2} , and were individually prepared at concentrations of 50,000-ppm (50-g/L) from the solid salts in distilled, deionized water. Solutions at 100, 500, 1,000, 5,000, and 10,000-ppm of mixed anions were then prepared by serial dilution from the 50,000-ppm stock solutions. All water used was de-ionized, reagent grade with 18-M Ω /cm resistance.

Instrumentation and Analytical Method

Perchlorate Analysis. Ion chromatography was performed on a Dionex DX-500 ion chromatograph system with a GP-40 Gradient Pump, CD-20 Conductivity Detector, a LC-20 Chromatography Enclosure, and an AS40 Automated sampler. The injection volume was 1 ml. Anion separation was obtained on a Dionex IonPac AS-16 separation column (4.0 x 250-mm) with an AG-16 guard column (4.0 x 50 mm) and an ATC-1 anion trap column. An EG-40 Eluent

Generator with a potassium hydroxide cartridge were used to generate the 35-mM KOH mobile phase. The mobile phase flow rate was set at 1.25 mL/min. Background suppression was achieved by using an Anion Self-Regenerating Suppressor (ASRS)-ULTRA suppressor.

The performance of the AS-16 was compared to that the AS-11 column. Anion separation was obtained on a Dionex IonPac AS-11 separation column (4.0 x 250-mm) with an AG-11 guard column (4.0 x 50 mm) and an ATC-1 anion trap column. The mobile phase for the AS-11 column consisted of 100-mM NaOH in water, with a flow rate of 1.0 ml/min.

For both AS-16 and AS-11 columns, the regenerant flow rate to the suppressor was 10 ml/min. The suppression current was set 300-mA, and analysis was performed at room temperature. All water used was deionized, reagent grade with 18-M Ω /cm resistivity or better. Dionex Peaknet software was used to perform the data processing. An Orion Research Model 701 A digital IONANALYZER was used for pH measurements.

Anion Analysis. Analysis of all anions other than perchlorate was performed on a Dionex DX-500 Microbore system, configured with a GP-40 gradient pump, an ASRS-ULTRA suppressor, an ED-40 conductivity detector and an AS-3500 Autosampler. The suppressor was set at 100 mA and was operated in external water mode. Samples were injected manually through a 25- μ L loop at a flow rate of 0.25 ml/min.

For the mixed anion study, the separation of BrO_3^- , Cl^- , ClO_3^- , I^- , PO_4^{3-} , NO_2^- , NO_3^- , SO_3^{2-} and SO_4^{2-} was attained with a Dionex IonPac AS-16 microbore analytical column (2 mm x 250 mm) and an AG-16 guard column (2 mm x 50 mm). The mobile phase consisted of 35-mM NaOH in distilled, deionized water.

For the individual anion study, Br^- , ClO_3^- , and Cl^- were analyzed on a Dionex IonPac AS-11 analytical microbore column (2 mm x 250 mm) and an AG-11 guard column (2 mm x 50 mm). Separation was achieved with a gradient program: 0.5-mM NaOH for 7 minutes, and then gradually increased to 38.5-mM NaOH over a period of 20 minutes.

Effects of Sample Preparation Method on Mixed Anions

For the mixed anion study, a stock artificial water matrix was prepared by combining 10 mg of $\text{S}_2\text{O}_3^{2-}$ and 600 mg of BrO_3^- , Cl^- , ClO_3^- , I^- , PO_4^{3-} , NO_2^- , NO_3^- , CO_2^- , SO_3^{2-} , and SO_4^{2-} in 1 L of distilled, deionized water for a total TDS of 6,610-ppm. Mixed anion samples at TDS levels

of 100, 500, and 1,000-ppm were prepared by serial dilution from the stock artificial water matrix.

Prior to sample analysis, a 2-ml mixed anion sample was filtered serially through an Ag On-Guard (Dionex) cartridge to exchange the interference cations onto the resin and form the insoluble silver salts of the interference anions. The samples were then filtered with the hydrogen On-Guard cartridges to remove excess silver cations that may have been released from the silver cartridge. A Millipore 0.45 μ M x 13 mm Millex-HV 13 Filter was used to filter out any resin or precipitated salts that remained in the sample. Samples were subsequently analyzed for perchlorate and anion concentrations using ion chromatography.

SECTION III: RESULTS

Method Development and Validation

Optimized chromatographic conditions were described in Section II. Baseline noise was kept minimal. Prior to analysis, the ion chromatography system was equilibrated to produce a background conductance less than 2 μS . To establish the baseline, system blanks (de-ionized water) were injected onto the system. The system blanks demonstrated that the IC system was free from contamination, showing negative baseline deflection between 2.2 to 3.2 minutes due to the void volume followed immediately by strong positive baseline deflection from the non-retained species. The chromatogram of a 100-ppb perchlorate standard obtained on a new standard bore AS-16 column, with EG-40 generated 35-mM KOH mobile phase flowing at 1.25 ml/min., showed one distinct peak around 12.5 minutes on a new column. As the column ages, perchlorate elution times decrease and eventually stabilize between 10.5-12.5 minutes. When 35-mM NaOH is used, rather than the EG-40 generated KOH, perchlorate eludes from the column between 17 and 18 minutes. Perchlorate retention time was established by injecting standards with increasing concentrations of perchlorate and observing the corresponding increase in the peak area counts. Peak identity was also verified by analyzing perchlorate standards from a second source.

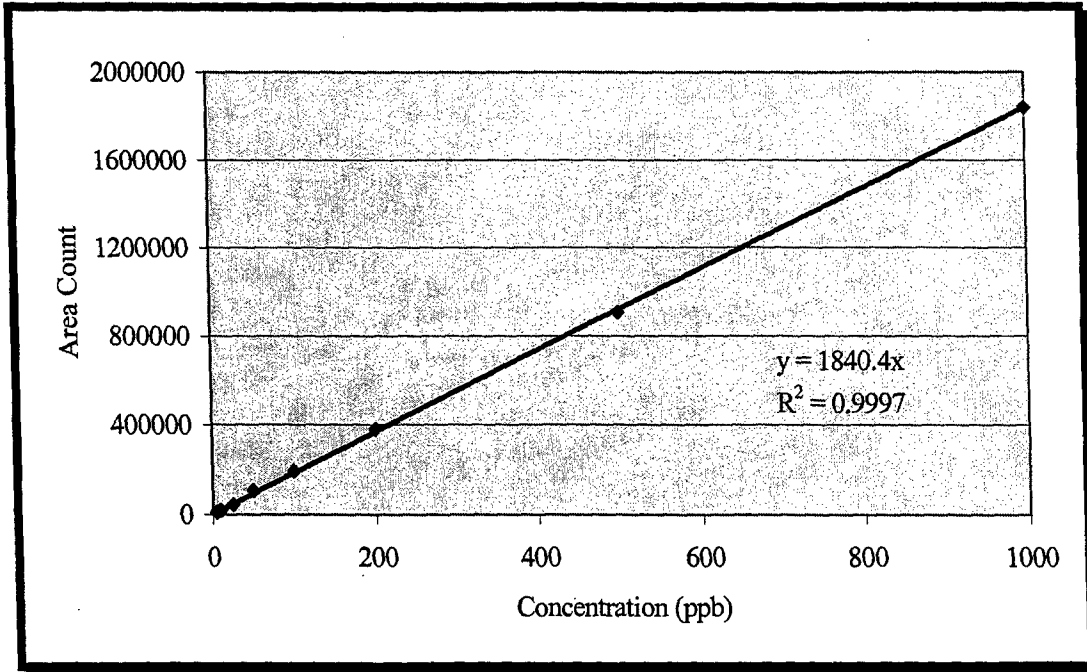
The method detection limit data for perchlorate was obtained on a new column with an EG-40 eluent generator. The method detection limit data is shown in Table 3.1. Eight replicates of 5-ppb perchlorate standards were analyzed over 72 hours. Per guidelines and procedures set forth in Code of Federal Regulations 40, Chapter 1, Pt. 136, Appendix B, the calculated method detection limit (MDL) is 0.19 $\mu\text{g/L}$ (ppb). The Student t-test value for eight samples ($n = 8$, degree of freedom = 7) at the 99% confidence limit is 2.998. At the calculated method detection limit, the perchlorate peak is well resolved and the signal to noise ratio is greater than 3. The calculated on-column limit is 0.19 ng ($0.1 \mu\text{g/L} \cdot 1000 \mu\text{L} = 1.94 \times 10^{-4} \mu\text{g}$). The practical quantitation limit at 10 times the MDL is 1.94 $\mu\text{g/L}$.

Table 3.1. Method detection limit data for perchlorate analysis on an AS-16 column. 35-mM KOH mobile phase, flowing at 1.25 mL/min.

Data Point	Concentration (ppb)	Area Count	Retention Time (min.)
1	5	9751	12.25
2	5	9687	12.32
3	5	9762	12.32
4	5	9556	12.38
5	5	9935	12.17
6	5	9874	12.17
7	5	9835	12.17
8	5	9635	12.17
Average		9754	12.24
Standard Deviation		118	0.08
Per		1%	0.5%
MDL		0.194	

Calibration curves were generated by plotting the concentrations of each standard against the peak area count obtained. To illustrate the ruggedness of the method, a typical calibration curve obtained on an aged AS-16 column (>1,200 injections) is shown in Figure 3.1. The calibration curve was linear through the calibration range, from MDL to 10,000 x MDL, over 5 orders of magnitude, and the calibration line was typically described by the equation $Y = 1840.4 X$. The correlation coefficient values were better than 0.9998. The slope of the line is directly related to the sensitivity of the ion chromatography system. The slopes of calibrations generated from sample batches were monitored over two months. During that period, over 1,200 standards, controls, and water samples were analyzed, and the slopes of the calibration lines were within 1% of the original calibration line, indicating the system response had little or no change. During the same two month period, method accuracy and method precision were also monitored. The method accuracy, which is measured as percentage of the known value, was between 90 and 110%. The method precision, which is measured as relative percent standard deviation, was better than 1%.

Figure 3.1. Calibration curve generated from standard curve shown in figure 3.2



Stack plots of the ion chromatograms obtained for perchlorate standards with concentrations from 5 to 1000- $\mu\text{g/L}$ on AS-16 and AS-11 columns are shown in Figures 3.2 and 3.3, respectively. For both the AS-16 and AS-11 columns, the plots were obtained after the columns had been in use for more than two months. The peak shapes of perchlorate standards from 5- to 1,000- $\mu\text{g/L}$ on the AS-16 column (Figure 3.2.) were highly symmetrical and well resolved, with little or no observed retention time shift in the chromatograms. In comparison, the AS-11 column showed increased peak tailing with increasing perchlorate concentrations. On the AS-11 column, the perchlorate retention time decreased as much as one minute, with a corresponding increase in perchlorate concentration, from 5 to 1000 $\mu\text{g/L}$.

Figure 3.2. A stack plot of 5 to 1000- $\mu\text{g/L}$ perchlorate calibration standards on an AS-16 column. Chromatographic conditions: 35-mM KOH with flow rate at 1.25 ml/min, 1000- μl injection volume

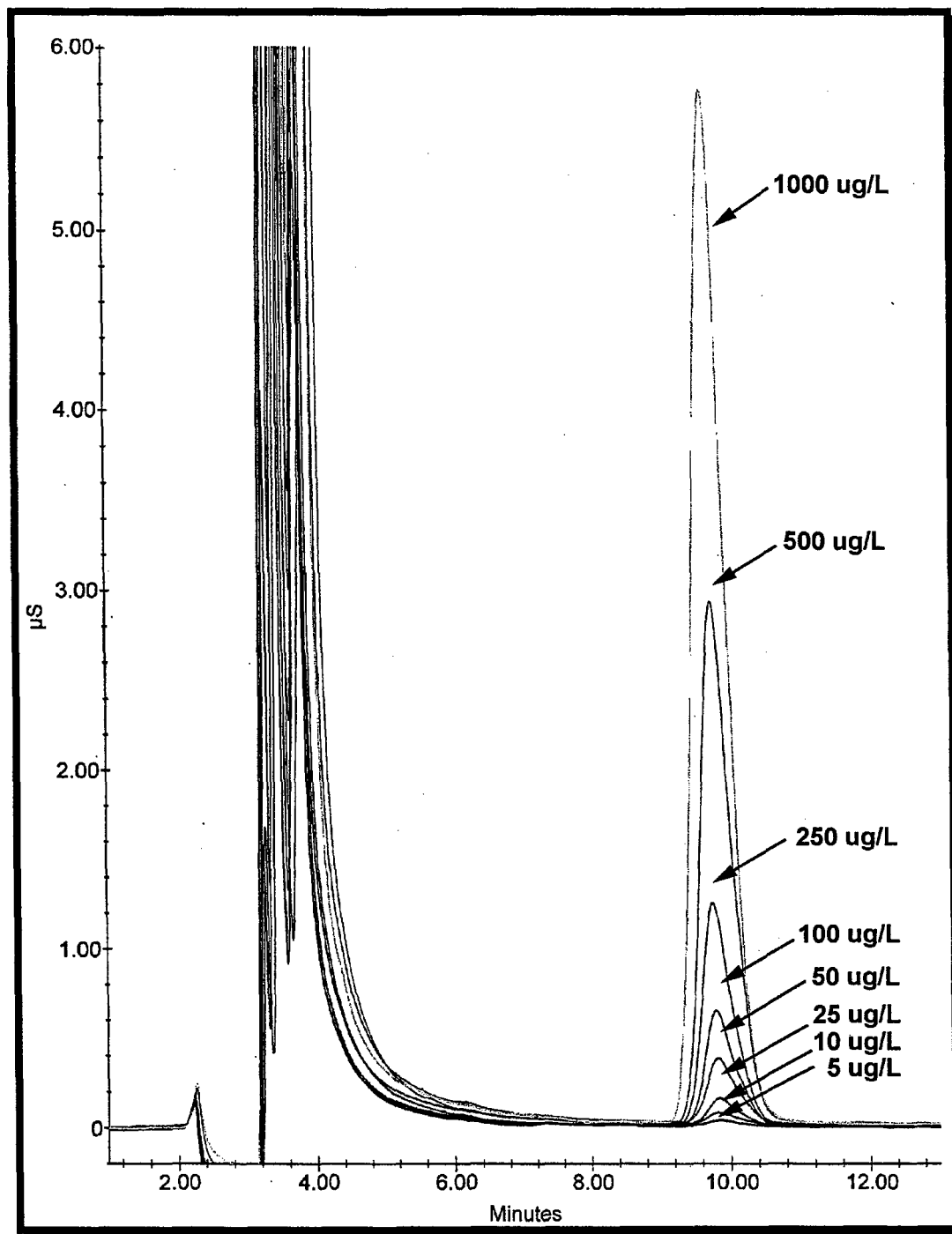
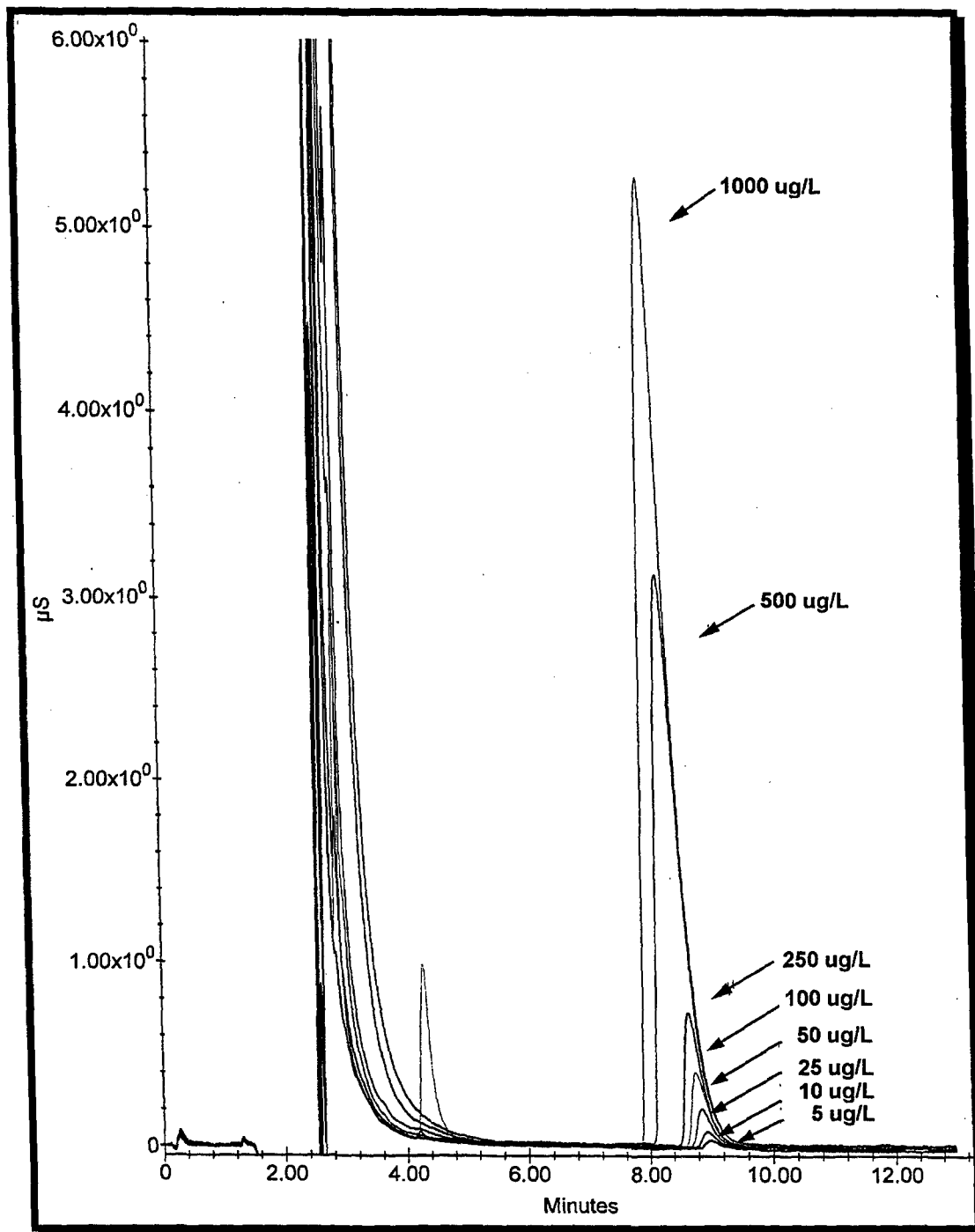


Figure 3.3. A stack plot of 5 to 1000- $\mu\text{g/l}$ perchlorate calibration standards on an AS-11 column. Chromatographic conditions: 100-mM NaOH with flow rate at 1.0 ml/min, 1000- μl injection volume



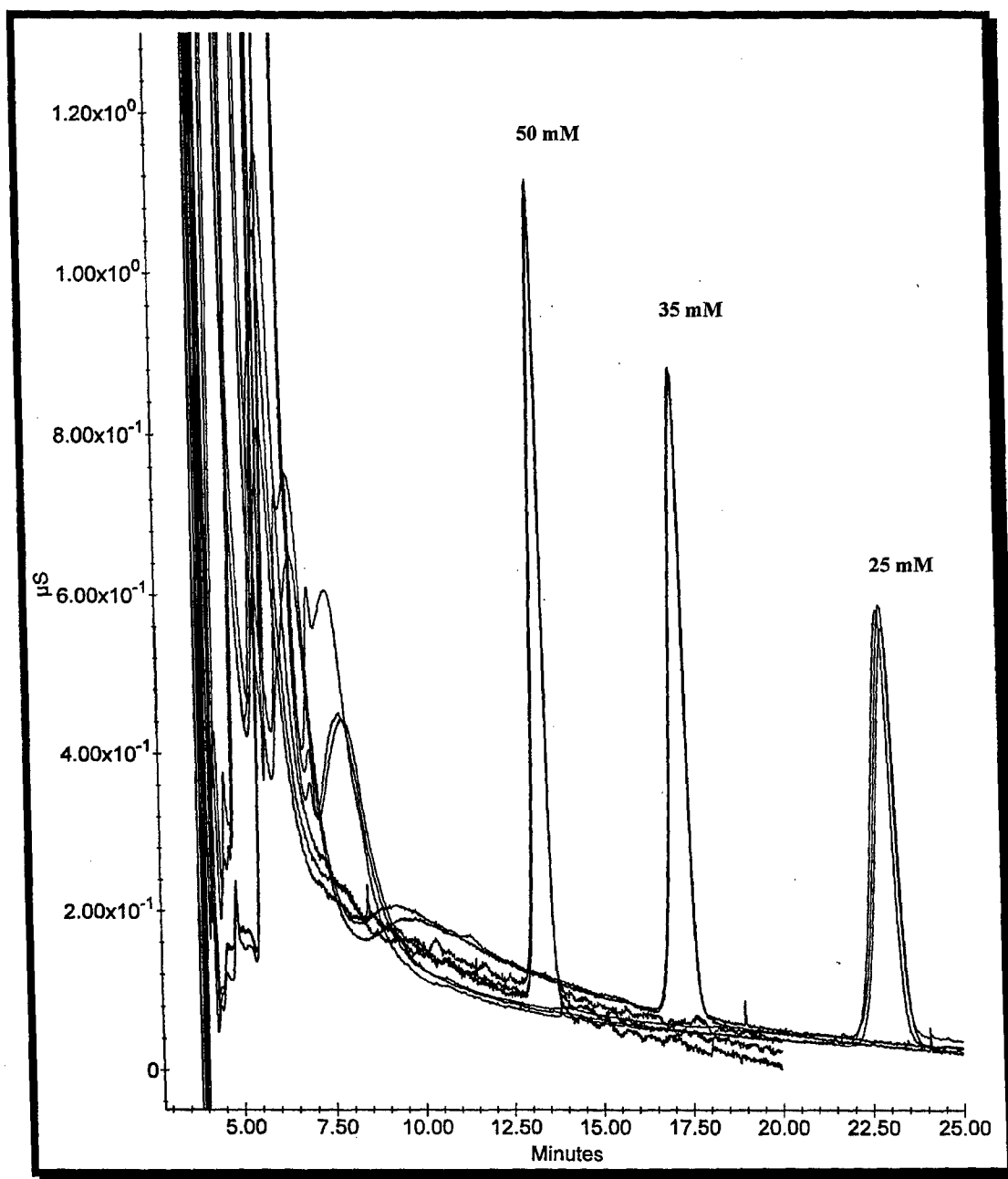
Effects of KOH Mobile Phase on Perchlorate Retention Time and Response

The effects of the potassium hydroxide mobile phase strength on the chromatography of 100-ppb perchlorate standards were examined on a new AS-16 separation column, AG-16 guard column, ATC-1 trap column, and an ASRS-Ultra suppressor. A stack plot of three 100-ppb perchlorate standards, analyzed with mobile phase concentrations at 25, 35, and 50-mM and flowing at 1.0 ml/min, is shown in Figure 3.4. With increasing KOH concentrations from 25 to 50-mM, perchlorate retention times were found to decrease from 22.9 to 13.35 minutes (Table 3.2). Peak area counts remain constant and detector response is unaffected with increasing KOH concentration, as peak height increases from 5,390 to 10,005, while peak width at half height decrease from 0.75 to 0.3 minutes. Figure 3.4 shows that at a flow rate of 1.0 ml/min, the best chromatographic results are obtained with 35-mM KOH, resulting in good symmetry and no apparent artifact. In comparison, perchlorate peak shape exhibits unacceptable peak broadening at 25-mM and peak fronting at 50-mM. The 17.25-minute perchlorate retention time on the AS-16 with 35-mM KOH at 1.0 ml/min is about 5 minutes longer than the 12-minute retention time obtained with recommended AS-11 method. However, the perchlorate retention time on the AS-16 was further optimized by increasing the flow rate of the mobile phase.

Table 3.2. Effects of KOH mobile phase strength on 100-ppb perchlorate retention time, area count, and peak height at 1.0 ml/min flow rate

	Retention Time	Retention Time	Retention Time	Average	Standard Deviation	Percent CV
25mM	22.98	22.93	22.85	22.92	0.1	0.2%
35mM	17.28	17.25	17.23	17.25	0.0	0.1%
50mM	13.37	13.35	13.33	13.35	0.0	0.1%
	Area Count	Area Count	Area Count	Average	Std Dev	%CV
25mM	204914	211280	211805	209333	3132	1.5%
35mM	228414	228617	229411	228814	430	0.2%
50mM	212344	211152	213629	212375	1011	0.5%
	Peak Height	Peak Height	Peak Height	Average	Std Dev	%CV
25mM	5259	5439	5473	5390	93.9	1.7%
35mM	8043	8053	8106	8067	27.6	0.3%
50mM	10031	9865	10119	10005	105.3	1.1%

Figure 3.4. Elution profile of 100-ppb perchlorate on an AS-16 column, 1.0-ml/min at 25, 35, and 50-mM KOH mobile phase



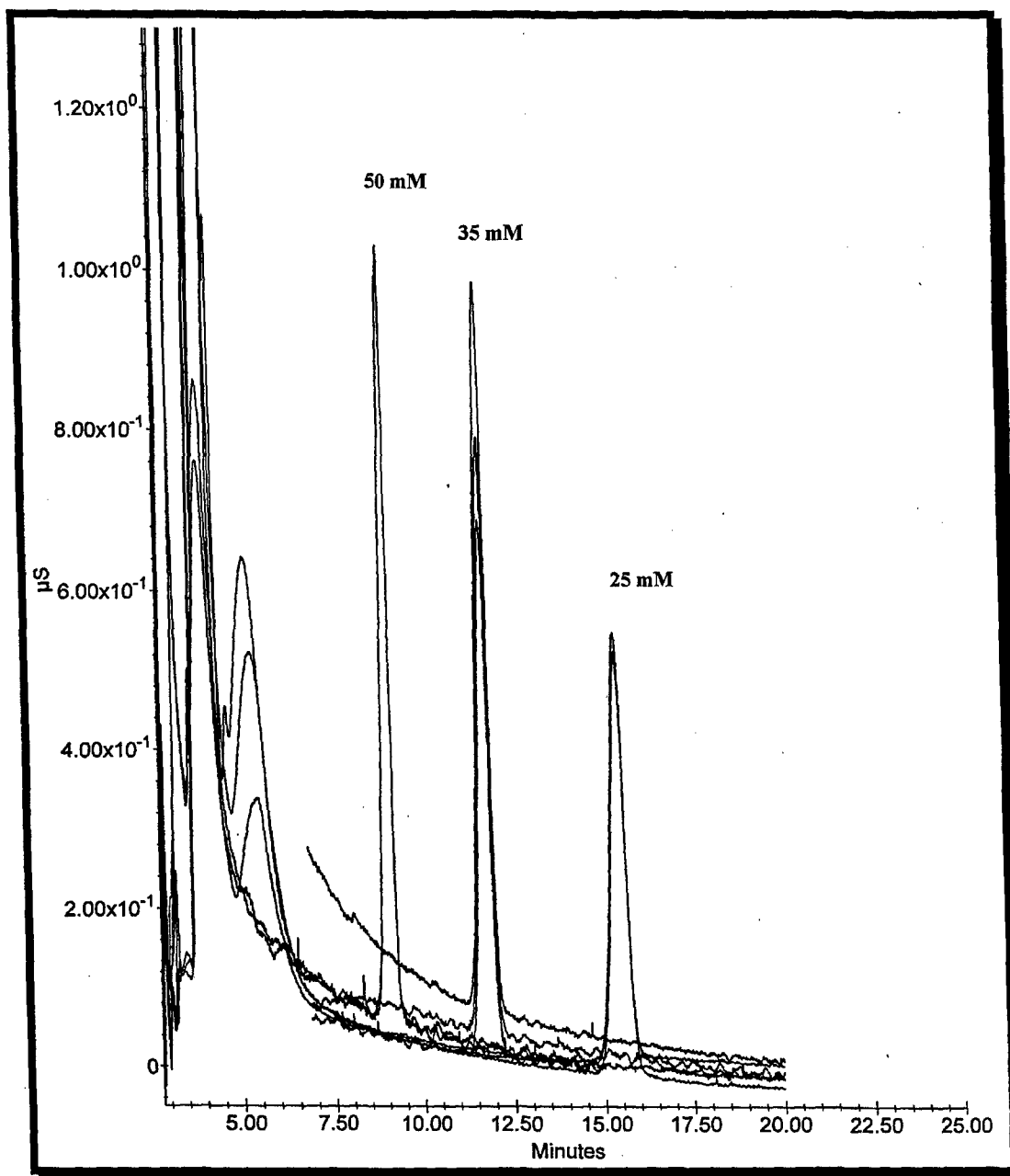
A stack plot of three 100-ppb perchlorate standards analyzed with KOH concentrations of 25, 35, and 50-mM, flowing at 1.0 ml/min is shown in Figure 3.5. The raw data is presented in Table 3.3. When the KOH concentration of the mobile phase was increased from 25 to 50-mM, the retention time of perchlorate decreased significantly from 15.45 to 9.05 minutes. The peak area

counts for perchlorate remained constant with changing KOH concentrations, though the shape of the perchlorate peak sharpened dramatically with increased KOH. Although the chromatography showed good peak symmetry at 1.5 ml/min in both the 35-mM and 50-mM KOH mobile phase, the 50-mM NaOH mobile phase causes the perchlorate peak to elute too quickly from the column. At 50-mM KOH, the perchlorate is not sufficiently separated from the non-retained anions. Hence, the optimized AS-16 chromatography condition was determined to be between 1.0 and 1.5 ml/min, or 1.25 ml/min, with a 35-mM KOH mobile phase. With the optimized conditions on a new AS-16 column, the perchlorate retention time should be 12.5 minutes, which is comparable to that of the AS-11 method. With aging, perchlorate retention time decreases to about 10 minutes.

Table 3.3. Effects of KOH mobile phase strength on 100-ppb perchlorate retention time, area count, and peak height at 1.5 ml/min flow rate

	Retention Time	Retention Time	Retention Time	Average	Standard Deviation	Percent CV
25mM	15.47	15.43	15.45	15.45	0.0	0.1%
35mM	11.77	11.78	11.78	11.78	0.0	0.0%
50mM	9.05	9.05	9.05	9.05	0.0	0.0%
	Area Count	Area Count	Area Count	Average	Std Dev	%CV
25mM	152131	143417	148873	148140	3595	2.4%
35mM	155642	155253	140904	150600	6858	4.6%
50mM	152830	149243	152157	151410	1557	1.0%
	Peak Height	Peak Height	Peak Height	Average	Std Dev	%CV
25mM	5351	5071	5323	5248	125.9	2.4%
35mM	7145	7399	6728	7091	276.6	3.9%
50mM	9542	9595	9671	9603	52.9	0.6%

Figure 3.5. Elution profile of 100-ppb perchlorate on an AS-16 column, 1.5 ml/min at 25, 35, and 50-mM KOH mobile phase



Effects of Sample pH on Perchlorate Recovery and Retention Time

The effect of sample pH on perchlorate recovery and retention time on the AS-16 column was examined by analyzing 50-ppb perchlorate standards ($n = 3$) prepared in 1, 5, 10, 20-mM NaOH and HCl. As shown in Table 3.4 and Figure 3.6, the retention times of the 50-ppb perchlorate standards decreased from 12.72 to 12.27 minutes, or 3.7% when the sodium hydroxide concentration was increased in the sample from 0 to 20 mM. An increase in sodium hydroxide sample concentration results in lower peak area counts, indicating decreased detector response. The effects of HCl on 50-ppb perchlorate standards are shown in Table 3.5 and Figure 3.7. When the hydrochloric acid concentration in the samples was increased from 0 to 20 mM, the retention time of perchlorate increased from 12.72 to 13.20 minutes, or 3.7% and detector response was diminished.

Table 3.4. Effects of NaOH concentrations on 50-ppb perchlorate response and retention time on an AS-16 column, 1.25 ml/min, and 35-mM KOH mobile phase

[NaOH] (mM)	Retention Time (min)	Area Count	Peak Height	Percent Area Count Difference (%)
0	12.72	114809	4285	0%
1	12.53	88928	3585	-23%
5	12.45	84974	3225	-26%
10	12.40	89691	3048	-22%
20	12.27	91218	2394	-21%

Table 3.5. Effects of HCl concentrations on 50-ppb perchlorate response and retention time on an AS-16 column, 1.25 ml/min, and 35-mM KOH mobile phase

[HCl] (mM)	Retention Time (min)	Area Count	Peak Height	Percent Area Count Difference (%)
0	12.72	114809	4285	0%
1	12.75	89611	3474	-22%
5	12.80	86485	3339	-25%
10	12.96	72743	3215	-37%
20	13.20	71151	3364	-38%

Figure 3.6. Elution profile of 50-ppb perchlorate spiked in various concentrations of NaOH on an AS-16 column with 35-mM KOH mobile phase flowing at 1.25 ml/min

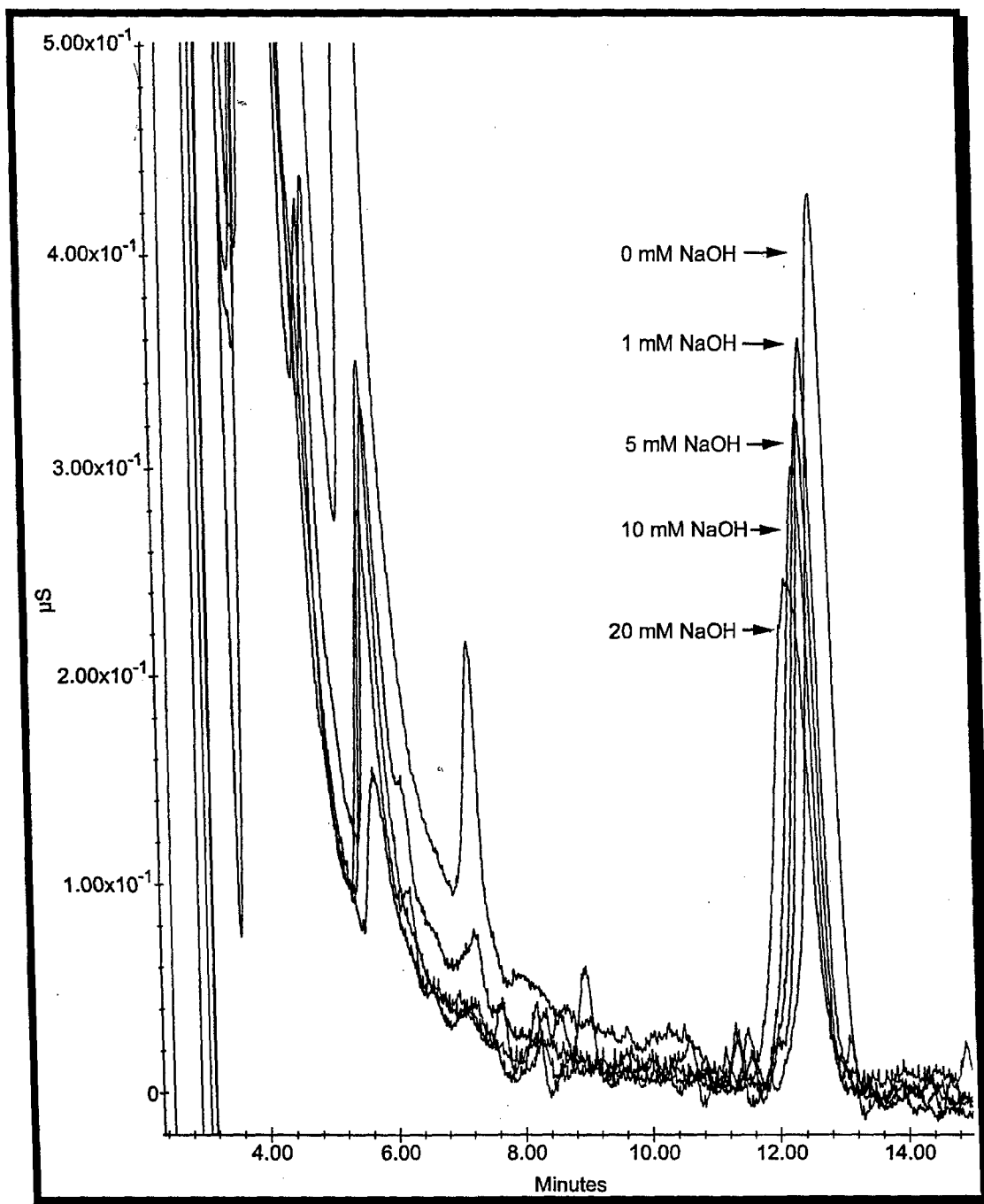
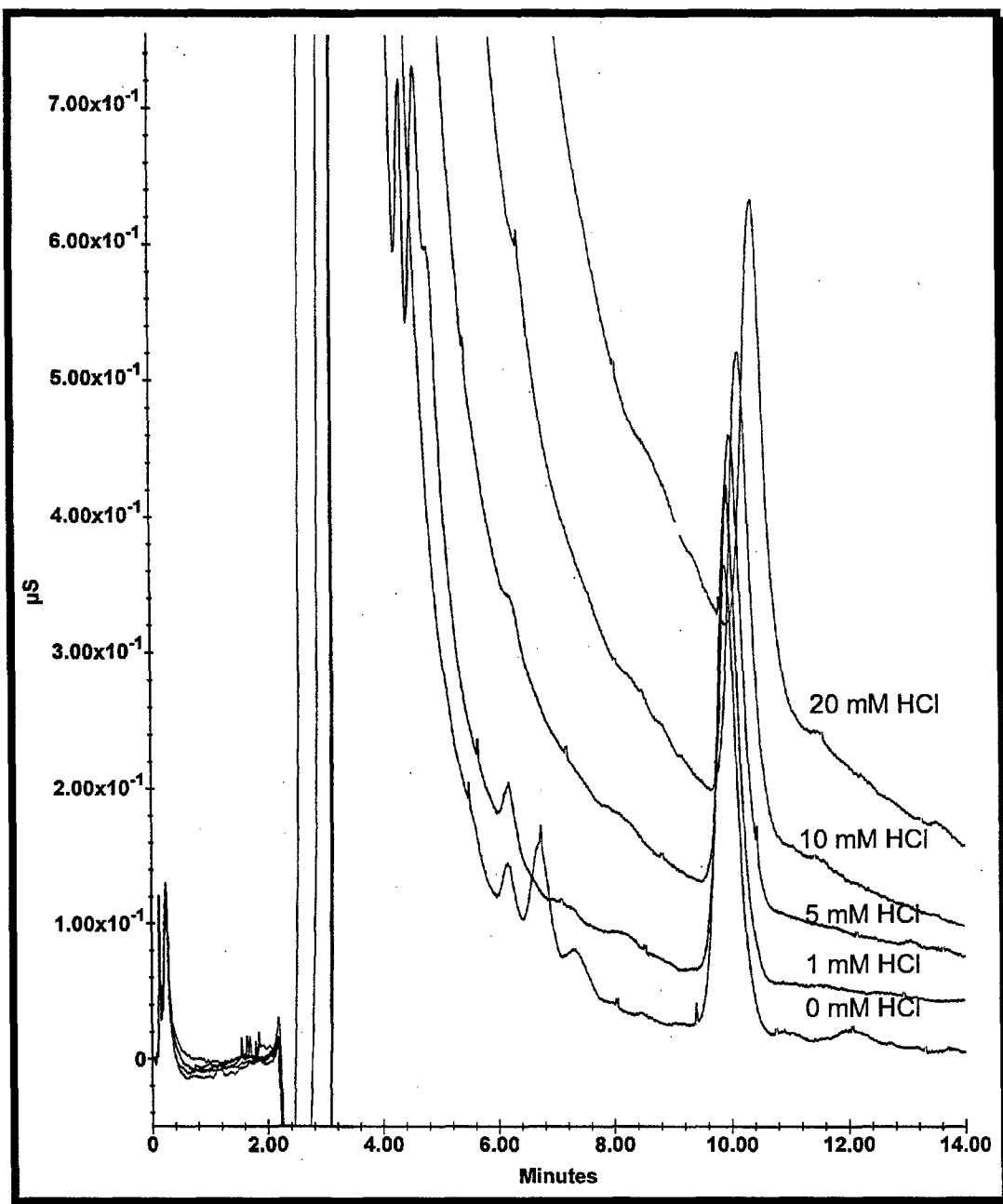


Figure 3.7. Elution profile of 50-ppb perchlorate spiked in various concentrations of NaOH on an AS-16 column with 35-mM KOH mobile phase flowing at 1.25 ml/min



Interference Study

Two different interference studies similar to those used by the ISPC when evaluating the AS-5 and AS-11 columns, were performed with the AS-16 method. In the first study, the same set of 22 anions tested by the IPSC were injected at the 100 ppb level (in the presence of 20-ppb perchlorate) on the AS-16 column, using the conditions described in the experimental section. Under the optimized conditions for perchlorate analysis on the AS-16 column, only cyanide, iodide and thiocyanate showed any significant retention on the AS-11 column (Table 3.6). Both cyanide and iodide have retention times around 9.45 minutes, and the retention time of thiocyanate is 10.87 minutes. Perchlorate shows clear resolution from all of the tested anions, and is separated by three minutes from thiocyanate, which is the nearest eluting anion and which would not be typically found at high levels in drinking water or ground water.

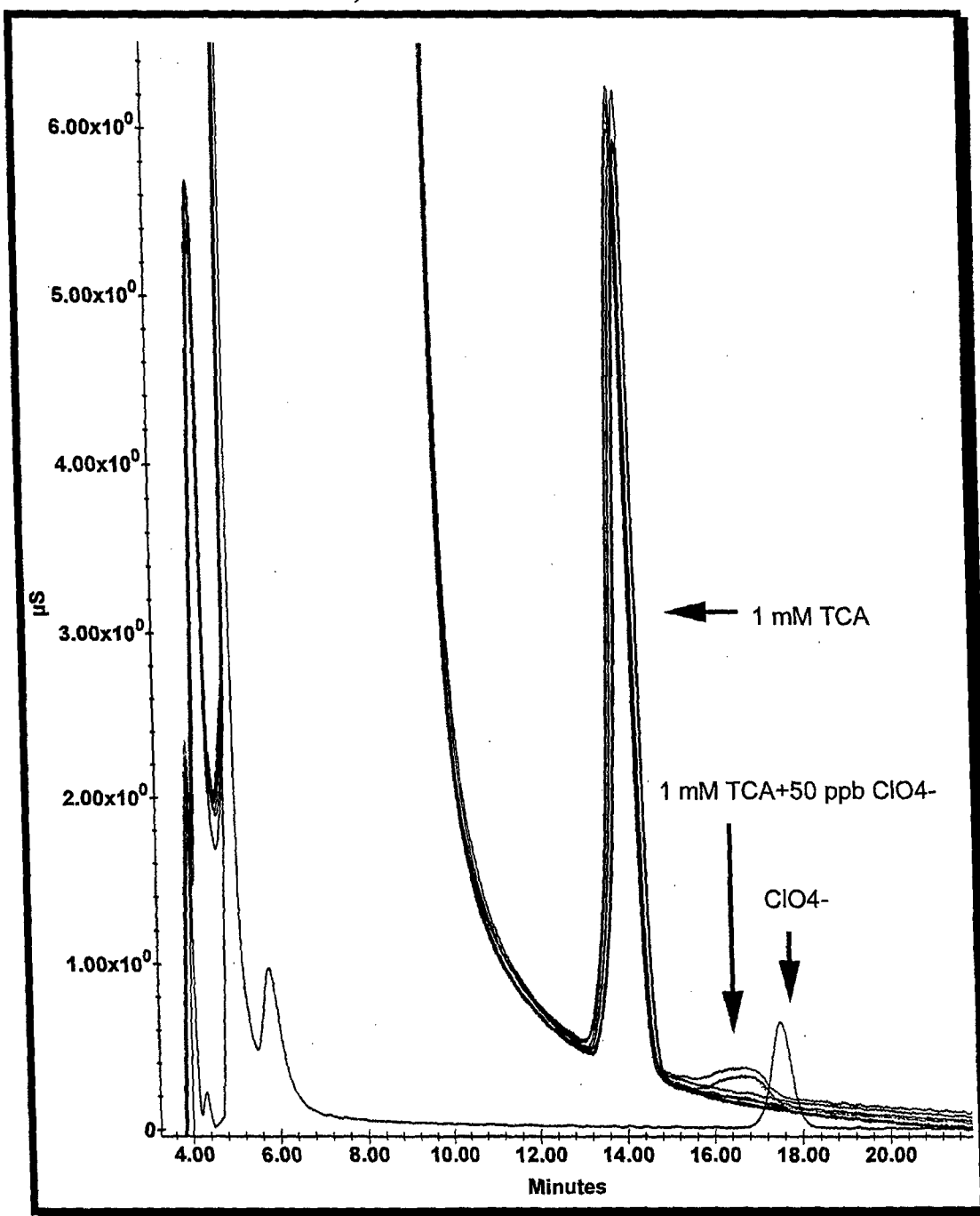
Table 3.6. Retention times of common inorganic anions on AS-16 column

Anion	Anion Retention Time (minutes)	Perchlorate Retention Time (minutes)
arsenate	<4	12.72
arsenite	<4	12.79
bromate	<4	12.84
bromide	<4	12.78
carbonate	<4	12.78
chlorate	<4	12.65
chloride	<4	12.70
chromate	<4	12.71
cyanide	9.32	12.71
humic acid	<4	12.72
iodate	<4	12.75
iodide	9.45	12.65
molybdate	<4	12.50
nitrate	<4	12.60
nitrite	<4	12.50
phosphate	<4	12.65
phthalate	<4	12.65
selenate	<4	12.55
sulfate	<4	12.50
sulfite	<4	12.50
thiocyanate	10.87	12.55
thiosulfate	<4	12.55

In addition to the inorganic chemicals listed in Table 3.6, the first study also examined the possible interference associated with the organic chemicals listed on page 5 of Section II. To examine the effects of the organics on perchlorate retention time and detector response, standards were prepared with each of the individual organic solvents at concentrations of 0, 100, and 1,000-ppb. Standards at each concentration level were then spiked with 25, 50, and 100-ppb perchlorate. Due to the volatile nature of the organics, samples containing the organic chemicals were carefully prepared in volumetric flasks and then transferred to vials with Teflon septa. Samples were analyzed within 24-48 hours of preparation. The organic interference study was performed in the absence of the EG-40 Eluent Generator. A 35-mM NaOH mobile phase was used at a flow rate of 1.5 ml/min, rather than the 35-mM KOH.

With the exception of trichloroacetic acid, none of the organic chemicals were shown to affect either the chromatography or the detector response for perchlorate. Figure 3.8 shows the effect of 1-mM trichloroacetic acid on the chromatography and detector response for 50-ppb perchlorate-spiked samples. As illustrated in Figure 3.8 the 50-ppb perchlorate peak was expected to appear around 17.2 minutes. In the absence of perchlorate, 1 mM TCA appeared as a single peak around 14.0 min. However, samples with both perchlorate and TCA showed one large peak at 14.0 min, corresponding to the TCA, and one broadened perchlorate peak at 16.5 min. The presence of trichloroacetic acid affects the chromatography of perchlorate on the AS-16 column by decreasing both the retention time and the detector response.

Figure 3.8. Effects of 1.0-mM trichloroacetic acid on the chromatography and detector response of 50-ppb perchlorate on an AS-16 Anion Separation Column with 35-mM NaOH, at 1.25 ml/min.



The second study examined the effect of the presence of a few common interference anions at high ppm levels on perchlorate recovery. Perchlorate standards at 50-ppb were

analyzed in the presence of 100, 500, 1,000, 2,500, 10,000, and 15,000-ppm chloride, carbonate, nitrate, and sulfate. As shown in Table 3.7, the presence of these common anions has no effect on the retention time. Furthermore, we did not observe any decrease in the percent recovery of 50-ppb perchlorate spikes.

Table 3.7. Effect of ppm levels of carbonate, nitrate, chloride, and sulfate anions on 50-ppb perchlorate recovery on the Dionex IonPac AS-16 column

Common Anion	Anion Concentration (ppm)	Perchlorate Retention Time (min.)	Perchlorate Recovery (%)
Carbonate	100	12.75	96.6
Carbonate	500	12.75	98.8
Carbonate	1,000	12.65	92.1
Carbonate	2,500	12.69	94.2
Carbonate	10,000	12.63	95.5
Carbonate	15,000	12.62	96.4
Nitrate	100	12.66	99.1
Nitrate	500	12.65	98.4
Nitrate	1,000	12.63	96.5
Nitrate	2,500	12.59	94.7
Nitrate	10,000	12.55	95.9
Nitrate	15,000	12.62	95.4
Chloride	100	12.73	92.2
Chloride	500	12.70	99.2
Chloride	1,000	12.66	98.7
Chloride	2,500	12.70	97.4
Chloride	10,000	12.63	98.6
Chloride	15,000	12.71	97.6
Sulfate	100	12.59	94.4
Sulfate	500	12.61	100.0
Sulfate	1,000	12.55	93.4
Sulfate	2,500	12.52	97.4
Sulfate	10,000	12.44	96.9
Sulfate	15,000	12.48	98.9

Application of AS-16 Method

In order to verify the accuracy of the AS-16 method, and to determine the feasibility of its use on real water samples, the AS-16 method was applied to the same water samples used by the ISPC collaborative study.⁷ The results are shown in Table 3.8. The AS-16 method showed

results comparable to those of the accepted AS-11 method. The two methods showed no more than 3.5% difference in perchlorate recovery.

Table 3.8. Analysis of IPSC Samples by AS-16 Method

Samples	Theoretical Concentration (ppb)	AS-16 Concentration (ppb)	AS-16 Percent Difference (%)
C1T1	0	0	0
C1T2	0	0	0
C1T3	0	0	0
C2T1	5.8	5.6	3.5
C2T2	5.8	6.0	3.4
C2T3	5.8	6.0	3.4
C3T1	17.9	18.4	2.8
C3T2	17.9	18.7	4.5
C3T3	17.9	18.1	1.0
C4T1	35.4	36.5	3.2
C4T2	36.1	36.2	2.8
C4T3	35.5	36.1	1.7
STO	50.8	51.5	1.4
QCS (50ppb)	50.0	51.7	3.4
20ppb check	20.0	20.2	1.0

Effects of Sample Preparation Method on Perchlorate Retention Time and Recovery

The effect of the sample preparation method involving the use of Ag-OnGuard, H-OnGuard, and Millex-V filtration cartridges and filters on perchlorate recovery was examined with the AS-16 method for perchlorate analysis. Standards were prepared at 25 and 100-ppb perchlorate, and were then filtered either with the Millex-V cartridges only, or with the Ag⁺, H⁺, and Millex-V cartridges before analysis. The data presented in Table 3.9 shows that the Millex-V syringe filters have no significant effect on the percent recovery or retention time of perchlorate. Triplicate analysis of 25 and 100-ppb perchlorate standards filtered through the syringe filter showed better than 95 to 105% recoveries, as compared to the unfiltered standards. Table 3.10 shows the effect of the sample preparation method on the recovery of perchlorate from spiked water standards. The sample preparation method does not interfere with the quantitative determination of trace level perchlorate. In all samples, nearly 100% recovery was achieved with little or no effect on perchlorate retention time.

Table 3. 9. Effects of Millipore Millex HV-13 Filter on 25 and 100-ppb Perchlorate Spike Recovery

Perchlorate Concentrations (ppb)	Retention Time (min)	Area Count	Measure Concentration (ppb)	Percent Recovery (%)
25	9.1	34034	24.0	96%
25	9.1	34166	24.1	96%
25	9.0	37053	26.1	104%
100	8.8	146164	102.9	103%
100	8.9	148607	104.7	105%
100	8.8	146407	103.1	103%

Table 3.10. Effects of Ag- and H-OnGuard Cartridges and Millipore Millex HV-13 Filter on 25 and 100-ppb Perchlorate Spike Recovery

Perchlorate Concentrations (ppb)	Retention Time (min)	Area Count	Measured Concentration (ppb)	Percent Recovery (%)
25 ppb	9.1	33641	23.7	95%
25 ppb	9.0	36057	25.4	102%
25 ppb	9.1	35511	25.0	100%
100 ppb	8.9	143313	100.9	101%
100 ppb	8.8	148614	104.7	105%

Effect of Sample Preparation on Interference Anions

The separation of bromate, chloride, chlorate, iodide, phosphate, nitrite, nitrate, sulfite, and sulfate was possible with the use of the AS-16 gradient method. Mixed anion samples at 100, 500, and 1,000-ppm were examined for the presence of the anions before and after the sample preparation method. The results for the mixed anion study are shown in Table 3.11. The actual amount (μg) of material was calculated by multiplying the measured concentration by the volume of the sample, where the sample volume was 2.0 ml.

Ion chromatography results indicate successful removal of the bromate, bromide, chloride, iodide, nitrite, and phosphate anions. Chlorate, nitrate, and sulfate were not removed by the sample preparation method. The amount of nitrate in the sample actually showed a slight (3.1%) increase after treatment with the sample preparation method, and the concentration of sulfate showed a 24% increase. Previous studies with the AS-11 column showed bromide to be 100% removed from solution with the On Guard cartridges (Table 3.11).

Table 3.11. Results for Mixed Anion Removal Study Using On Guard Cartridges

Anion	Expected Concentration (ppm)	Expected Amount (µg)	Measured Final Concentration (ppm)	Measured Final Amount (µg)	Percent Removal (%)
NO2	5.65	11.3	1.13	2.26	80.0
	39.8	79.6	0.50	1.01	98.7
	87.6	175.3	ND	ND	100
NO3	7.81	15.6	6.38	12.8	18.2
	36.9	73.8	43.3	86.7	-17.5
	80.2	160.4	88.1	176.3	-9.91
PO4	4.79	9.57	3.76	7.53	21.4
	23.4	46.7	8.15	16.3	65.1
	51.9	103.9	11.6	23.3	77.6
S04	4.46	8.92	7.74	15.5	-73.5
	31.4	62.9	33.9	67.7	-7.76
	71.8	143.7	65.2	130.3	9.26
BrO3	6.92	13.8	5.74	11.5	17.0
	40.9	81.8	ND	ND	100
	84.1	168.3	ND	ND	100
Cl	7.18	14.4	3.09	6.18	56.9
	26.1	52.3	5.49	10.9	79.0
	53.5	107.2	9.49	19.0	82.3
ClO3	5.21	10.4	5.23	10.5	-0.49
	41.3	82.5	41.2	82.5	0.09
	91.1	182.1	89.4	178.8	1.82
I	5.18	10.4	ND	ND	100
	34.6	69.2	ND	ND	100
	85.3	170.6	ND	ND	100

A few individual anions were also examined at high TDS concentrations, in order to determine the capacity of the On Guard cartridges and to verify earlier results. Standards were prepared of chloride, chlorate, and bromide concentrations of 1,000, 5,000, and 10,000-ppm, and were analyzed with ion chromatography after treatment with the exchange cartridges. Table 3.12 shows the results obtained using the AS-11 gradient method. Chloride and bromide were

effectively removed from solution with the cartridges at concentrations as high as 10,000-ppm:

Chlorate, as previously shown, is not removed with the sample preparation method.

Table 3.12. Results for Individual Anion Removal Study Using On Guard Cartridges

Anion	Initial Concentration (ppm)	Final Concentration (ppm)	Percent Removal (%)
Bromide	1000	1.34	99.9
	5000	3.83	99.9
	10000	14	99.8
Chlorine	1000	0.89	99.9
	5000	155	95.9
	10000	1619	83.8
Chlorate	1000	728	27
	5000	4956	0.8
	10000	9083	9

SECTION IV: DISCUSSION AND CONCLUSIONS

A sensitive, selective, and robust ion chromatography method and an accompanied sample clean up procedure have been developed for perchlorate analysis with a Dionex AS-16 Separation Column. The method detection limit and reporting limit for perchlorate with this method are 0.19 $\mu\text{g/L}$ and 1.9 $\mu\text{g/L}$, respectively. This method shows greater sensitivity than both the AS-11 and AS-5 methods, which have reported method detection limits of 0.5 $\mu\text{g/ml}$ and 1.0 $\mu\text{g/ml}$, respectively.

The proposed AS-16 method has a higher capacity for applications such as industrial and wastewater samples, which contain high concentrations of contaminants. It was found from the interference study that high levels of inorganic anions that are commonly found in wastewater and other environmental samples do not interfere with the chromatographic separation and detection of perchlorate by the AS-16 method. Of the inorganic anions tested, only three showed any appreciable retention on the AS-16 column, and none interfered with either the retention time or the separation and recovery of perchlorate. It was also shown that 50-ppb perchlorate could be accurately quantified in the presence of up to 15,000-ppm carbonate, sulfate, chloride, or nitrate. Similar experiments performed at this laboratory with the AS-11 column have shown that 50-ppb perchlorate spiked at up to approximately 7,000-ppm of the anions could not be detected on an AS-11 column.

Among the organic solvents tested, trichloroacetic acid was the only organic solvent reported to interfere with perchlorate analysis on the AS-16 column. The presence of TCA in environmental samples not only distorts the perchlorate peak shape but also decreases both the retention time and recovery of perchlorate. TCA, DCA, and MCA are found in the environment typically as the by-products of chlorinating surface water with humic acids. Humic acids are usually found from the natural degradation of plant materials. Hence, in the future, special consideration should take into account when developing ion chromatography method specifically for analyzing perchlorate in the plant tissues. The other tested organic solvents did not interfere with the retention time or detector response.

Since some extraction techniques that are used in removing perchlorate from various natural settings involve the use of either HCl or NaOH in the sample preparation, the effect of sample pH on perchlorate recovery was examined. It was shown in this study, that with an increase in NaOH or HCl content in the sample, the perchlorate recovery was reduced by as much as 21% and 38%, respectively. When the pH of the perchlorate sample is varied from 7, the sensitivity of the AS-16 method is diminished. Consequently, when an acid or base is required for perchlorate extraction, it is necessary to prepare the control standards in the same manner as the extracted samples. Failure to maintain controls and environmental samples at the same pH level would yield inaccurate results.

The sample preparation method is useful in allowing the analysis of trace level perchlorate in environmental matrices that contain high levels of contamination. It is possible, with the silver and hydrogen On-Guard cartridges, to remove many of the interference anions from solution without removing any perchlorate. The sample preparation method did not affect the recovery of perchlorate with the AS-16 method. However, the cartridges effectively remove several of the anions commonly found in water, with almost 100% removal of chloride, bromide, iodide, bromate, nitrite, and phosphate.

The slight increase in nitrate concentration is probably due to the manufacturing process in which the silver cations are exchanged onto the resin. The most likely manufacturing procedure involves flushing the resin with silver nitrate, which could lead to some nitrate contamination in the resin. However, the presence of nitrate should not interfere with perchlorate analysis, as it is easily separated through chromatography. The increase in sulfate concentration may also be due to contamination by the resin. The resin contains sulfonyl groups, which act as exchange sites. It is possible that as the solution is pushed through the resin, some sulfate contamination is added to the sample. Again, the slight increase in sulfate should not interfere with perchlorate measurements, since the sulfate can be separated from perchlorate through ion chromatography.

In spite of the ease in handling and minimal preparation time, the advantages of using the commercially prepared silver and hydrogen On Guard cartridges are counter-balanced by their relatively high cost. It is possible to prepare a silver-saturated exchange resin in-house by

flushing Dowex AG50w-x8 cation exchange resin with a dilute silver nitrate solution. This resin was effective in the removal of the same interference anions that are removed with the cartridges. However, it is more likely to leave nitrate in the sample, and it has a greater potential for perchlorate loss than the cartridges due to difficulty in sample transfer.

SECTION V: REFERENCES

1. Las Vegas Sun, September 23, 1997
2. Las Vegas Sun, September 24-25, 1997
3. Las Vegas Sun, September 20, 1997
4. Las Vegas Sun, September 8, 1997
5. Las Vegas Sun, October 3, 1997
6. Las Vegas Sun, January 27, 1998
7. Chaudhuri, S., Okamoto, H., Pia, Steve, Tsui, D. "Collaborative Study on AS-5 and AS-11 Methods," in Inter-Agency Perchlorate Steering Committee Analytical Subcommittee Report, 26 March 1999.
8. "Standard Operating Procedure for Perchlorate." EPA Office of Water,
<http://www.epa.gov/OGWDW/ccl/perchlor/perchlo.html>.
9. California Department of Health Services, Sanitation and Radiation Laboratories Branch. Determination of Perchlorate by Ion Chromatography. Rev. 0, June 3, 1997.
10. Dionex Application Note 121, Dionex Corporation, Sunnyvale, CA, 1998
11. Jackson, P. et. Al. American Laboratory, April 1998.
12. Weast, R. C., Astle, M. J., Beyer, W. H. CRC Handbook of Chemistry and Physics. CRC Press, Inc. Boca Raton, Florida, p.p. B68 – B146.

SECTION VI: ACKNOWLEDGEMENTS

The authors thank Dr. Peter Jackson (Dionex Corporation, Sunnyvale, California) and his department for his generous technical support. We also like to thank Dr. Sanwat Chaudhuri (Utah Department of Health, Division of Epidemiology and Laboratory Services) for providing the organics chemicals used in the interference study.